

WASTES INTO PRODUCTION

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EFFECT OF METALLURGICAL SLAGS ON THE DRYING PROPERTIES OF CERAMIC BODIES FOR THE PRODUCTION OF FACING BRICK PRODUCTION

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The effect of metallurgical slag on the drying properties of ceramic bodies is investigated. It is shown experimentally that fine-grain slag makes the raw clay material less sensitive to drying. It is confirmed by means of electron microscopy, infrared spectroscopy and simultaneous thermal analysis that slag grains possess a highly developed porous surface. As a result some of the water introduced during the formation of ceramic bodies is adsorbed on the surface of the slag grains. It is shown that fine-grain metallurgical slag is an effective thinner in ceramic bodies.

Key words: drying, coefficient of drying sensitivity, air shrinkage, metallurgical slag.

Ceramic facing brick is usually produced by the plastic method. But, articles used as facing must meet exacting aesthetic requirements and in this connection optimization of the drying regime for defect-free products is one of the most important technological problems. The main factors affecting the drying time and quality of articles are the composition of the ceramic body, the conditions of processing and molding of the clay mass and the parameters of the drying regime — the temperature, moisture content and velocity of the coolant [1, 2].

Cracking of ceramic articles is an impediment to quickening the drying process. This is because stresses above a maximum admissible level determined by the strength of the material develop in the interior volume of an article [3]. The variation of the moisture content over the thickness of an article and the attendant air shrinkage are the main criteria for evaluating such internal stresses.

The use of mathematical models for describing the behavior of materials and articles tested under prescribed conditions is substantiated in the scientific literature on the control of technological processes [4, 5]. This is because mathematical modeling is much less energy and labor intensive than performing experiments to study processes and materials, and what is more the model developed and the accuracy

of the results obtained are adequate. By analyzing the planar stress state in a green brick by means of mathematical models it is possible to evaluate the efficacy of various thinning agents added to the batch and the probability of crack formation based on the established values of the maximum admissible normal and tangential stresses. Crack resistance is determined on the basis of the following conditions:

$$\begin{cases} \sigma_x^i \leq \sigma_x^{\max}, \\ \sigma_y^i \leq \sigma_y^{\max}, \\ \sigma_{xy}^i \leq \tau_{xy}^{\max}, \end{cases}$$

where σ_x^i , σ_y^i , σ_x^{\max} and σ_y^{\max} are, respectively, the values of the normal stresses in a sample having the i th composition and the maximum admissible normal stresses and τ_{xy}^i and τ_{xy}^{\max} are, respectively, the values of the tangential stresses in a sample having the i th composition and the maximum admissible tangential stresses.

The optimal drying regime can be secured by using scientifically substantiated raw materials and their ratio in the ceramic body [6]. When low-grade loamy clays, distinguished by high drying sensitivity, are used as the initial clay material, additional measures must be taken to improve the drying characteristics of the articles. A predominance of montmorillonite in the clay fraction promotes cracking and

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TABLE 1. Compositions of Ceramic Bodies

Composition No.	Component content, wt. %				
	Clayey raw material		Thinners		
	Vlasovskoe loamy clay	VKS-2 clay	Sand	Cast slag	Fine-grain slag
1.0	85.0	15.0	—	—	—
1.1	72.5	12.5	15	—	—
1.2	72.5	12.5	—	15	—
1.3	72.5	12.5	—	—	15

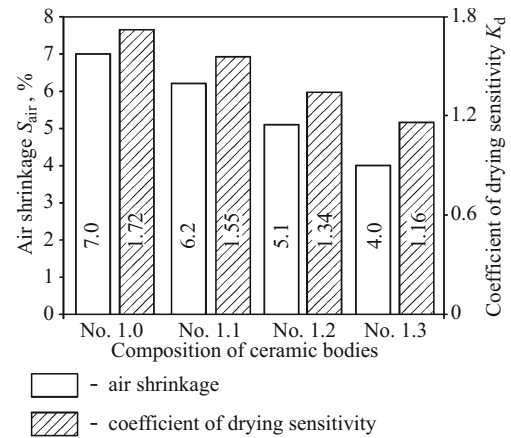
the formation of hairline cracks on the facing surface of a green part during drying. This makes it necessary to implement additional technological measures to reduce drying sensitivity and air shrinkage of articles.

Such measures can include thinning with sand, mild drying regimes, water-absorbing additives, increasing the water conductivity of the clay body, careful preparation of the batch to achieve a high degree of homogenization and so forth. The presence in different regions of the country of a large amount of thinning materials permits wide use clay thinning in production practice by introducing non-shrinking natural or technogenic additives, such as quartz sand, fire-clay, dehydrated clay, ashes, slag and others. In this connection the actual problem is to provide scientific substantiation for the choice of thinning materials used to optimize the drying regime for a green article.

The aim of the present work is to optimize the drying properties of facing brick based on clay material using natural and technogenic thinners, determine by means of a complex of physical and chemical investigations the mechanism of the reduction in the drying sensitivity of clay raw material when using fine-grain metallurgical slag as a thinner.

To find the optimal thinning component a series of experiments was conducted to determine the drying properties of samples fabricated using batches based on clay raw materials together with thinning materials. Loamy clay from the Vlasovskoe deposit (plasticity $P = 13.6$) together with VKS-2 refractory clay from the Vladimirovskoe deposit with plasticity $P = 14.0$ in the ratio 85 : 15, respectively, was used as the plastic component. Sand from the Vladimirovskoe deposit (VKTG, JSC) and metallurgical slags — cast and fine-grain, obtained during the production of steel in electric steel-making furnaces — were used as thinners. The compositions of the ceramic pastes are presented in Table 1.

To investigate the drying properties samples with linear dimensions $110 \times 110 \times 6$ mm were molded using the ceramic bodies presented in Table 1. The drying properties of the samples were determined using standard procedures. Before molding the components were subjected to a preparation procedure which included grinding the cast slag and passing it through a No. 09 sieve. The granulometric composition of the fine-grain slag is represented by the predominant fraction

**Fig. 1.** Air shrinkage and coefficient of drying sensitivity (according to A. F. Chizhskii) of the experimental bodies.

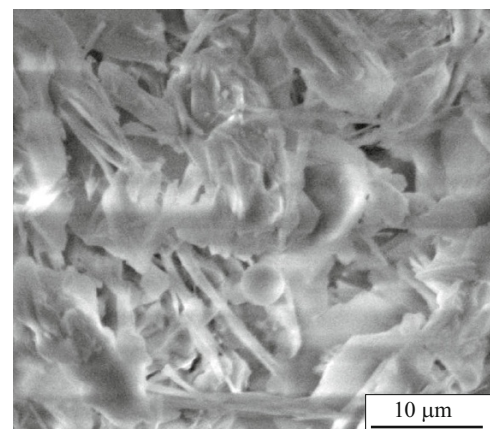
with grain size smaller than 1 mm, as a result of which the slag was introduced into the batch without additional comminution. The molding moisture content was 20% for samples fabricated using sand and cast slag and 22% using fine-grain slag.

The results obtained for the properties of ceramic samples are presented in Fig. 1. The samples with composition No. 1.3, fabricated using fine-grain metallurgical slag, have the lowest air drying indices and coefficient of drying sensitivity.

A complex of physical and chemical studies was implemented to study the mechanism responsible for the reduction of the drying sensitivity of clayey raw material when using fine-grain slag.

Electron microscopy showed that the surface of the grains of the experimental fine-grain metallurgical slag is characterized by a highly developed porous structure (Fig. 2).

The IR spectra of samples fabricated from clayey raw material with no additives (No. 1.0) and with fine-grain metallurgical slag added (No. 1.3) are presented in Fig. 3. It is

**Fig. 2.** Electron-microscopic image of the surface of fine-grain metallurgical slag ($\times 5000$).

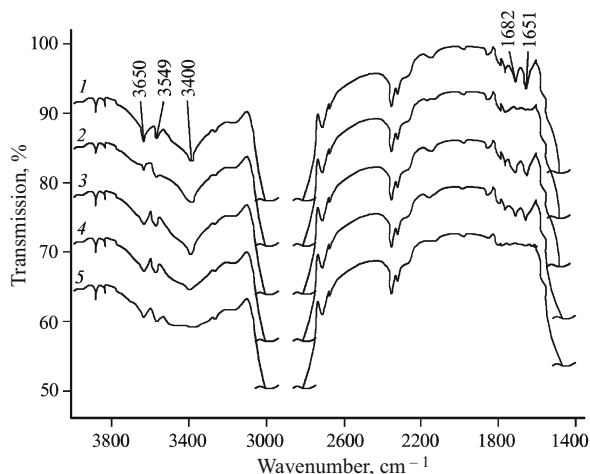


Fig. 3. IR spectra of samples from ceramic pastes No. 1.0 and 1.3 for different drying temperatures t_d : 1) No. 1.0, $t_d = 20^\circ\text{C}$; 2) No. 1.0, $t_d = 100^\circ\text{C}$; 3) No. 1.3, $t_d = 100^\circ\text{C}$; 4) No. 1.3, $t_d = 150^\circ\text{C}$; 5) No. 1.3, $t_d = 250^\circ\text{C}$.

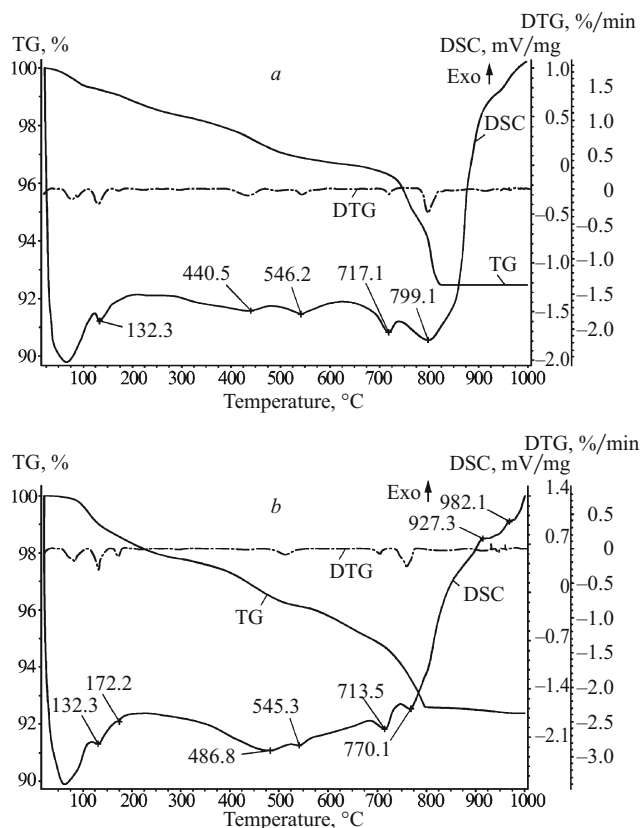


Fig. 4. DTA curves for the compositions No. 1 (a) and No. 1.3 (b).

evident from this figure that the peaks at 1682.220 and 1651.182 cm^{-1} , characteristic for the deformation vibrations of water, in samples fabricated using fine-grain slag are present up to temperature 150°C. The presence of IR peaks due

to the deformation vibrations of water can be explained by the fact that water introduced during the molding of the samples is adsorbed on the surface of slag grains and is removed only at temperatures above 150°C (Fig. 3, curve 5).

The samples Nos. 1.0 and 1.3 were investigated to study in greater detail by simultaneous thermal analysis (STA) the water removal occurring from ceramic pastes when they are heated. The temperature increased at the rate 10 K/min, the temperature measurement range was 25 – 100°C and the medium in the furnace was oxidative. The heating was done in a corundum crucible. The STA results are presented in Fig. 4.

The DSC curve of the sample No. 1.0 (Fig. 4a) is characterized by the following endo effects: 132.3°C — the removal of adsorption water; 440.5, 546.2 and 717.1°C — the removal of constitution water from clayey minerals; 799.1°C — dissociation of calcium carbonate. The presence of an endo effect at 172.2°C on the DSC curve for sample No. 1.3 (Fig. 4b), containing fine-grain metallurgical slag, confirms that the release of adsorption water from the pores in the slag starts at this temperature. The endothermal effect at 132.3°C corresponds to the removal of adsorption water, at 446.8, 545.3 and 713.5°C to the removal of constitution water from clayey minerals and at 770.1°C to the dissociation of calcium carbonate present in the clayey raw material. Two exothermal effects due to the crystallization of new phases are observed: one at 927.3 and the other at 982.1°C. Analysis of the thermogravimetric curves shows that the sample No. 1.3 compared with the sample with base composition No. 1.0 is characterized by greater mass loss (by 0.5%) in the temperature interval 25 – 400°C.

In summary, the mechanism of the release of adsorption moisture from the surface of the grains of metallurgical slag is similar to the action of water absorbing additives and zeolite rocks, in which the water introduced during the molding process fills the pores and intracrystalline channels of the thinner. It is noted in [7] that the removal of intrapore zeolitic water occurs in the temperature range 150 – 400°C with the initial structure of the mineral remaining undisturbed. This fact is of great practical significance for coarse-grain ceramic bodies based on high-sensitivity clayey raw material. It was established experimentally that fine-grain metallurgical slag used as an additive significantly reduces the drying sensitivity (by a factor of 1.5) compared with samples based on pure clayey raw materials with no additives. The metallurgical slag studied in the present work can be recommended for use as a highly effective thinning component in coarse-grain ceramic pastes.

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